



Quantification and characterization of dissolved organic carbon and iron in sedimentary porewater from Green Bay, WI, USA

EDWARD J. O'LOUGHLIN^{1,3,*} and YU-PING CHIN²

¹*Environmental Science Program, Ohio State University, Columbus, OH 43210-1086, USA;*

²*Department of Geological Sciences, Ohio State University, Columbus, OH 43210-1086, USA;*

³*Environmental Research Division, Argonne National Laboratory, Argonne, IL 60439-4843, USA;*

**Author for correspondence (e-mail: oloughlin@anl.gov)*

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Abstract. Both dissolved organic carbon (DOC) and iron play an important role in biogeochemical processes in lacustrine benthic environments. Moreover, recent evidence has shown that both substances can act as active reductants in the redox transformation of organic pollutants. This paper examines the nature and abundance of DOC and dissolved ferrous iron (Fe^{II}) in porewaters from a sediment core collected in Green Bay, WI, USA. The concentration of dissolved Fe^{II} and the abundance, absorbance at 280 nm ($A_{280\text{ nm}}$), molar absorptivities ($\epsilon_{280\text{ nm}}$), molecular weights, and polydispersities of DOC were measured as a function of depth in porewaters. Dissolved Fe^{II} concentrations increased from 3.6 μM near the sediment–water interface to 163 μM at a depth of 11 cm, then gradually declined. The DOC distribution varied with sediment depth, with the greatest variation in porewater DOC content and properties occurring in the transitional zone between oxic and suboxic conditions. The down-core porewater DOC profile was characterized by an increase in DOC concentration with depth from 0.64 mM OC at 1 cm to 1.23 mM OC at 13 cm, below which it remained relatively constant. A strong correlation was observed between Fe^{II} and DOC concentrations, suggesting that these constituents co-accumulate in these porewaters. The correlation between the DOC concentration of the porewaters and $A_{280\text{ nm}}$ was significant, making this parameter a good predictor for DOC concentrations in these waters. The molecular weight distributions of the porewater DOC were primarily monomodal, with relatively low polydispersities. Weight-average molecular weights ranged from 1505 to 1949 Da. This data set is unique in that it is the first detailed study of a relatively highly resolved DOC profile of benthic porewater in surficial sediment from the Laurentian Great Lakes.

Introduction

Dissolved organic carbon (DOC) in sedimentary porewater plays a significant role in many biogeochemical processes in aquatic environments, including the flux of sedimentary organic carbon to the overlying water (Alperin et al. 1999; Burdige et al. 1999); the remineralization and preservation of organic matter (Alperin et al. 1994; Hedges and Keil 1995; Burdige et al. 1999); and the distribution (Brownawell and Farrington 1986; Capel and Eisenreich 1990;

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Chin and Gschwend 1992; Mitra and Dickhut 1999), mobility (Thoma et al. 1991; Valsaraj and Sojitra 1997; Skrabal et al. 2000), and bioavailability (Harkey et al. 1994; Forbes et al. 1998) of contaminants. The porewater DOC pool is composed of an array of organic compounds that are often operationally grouped on the basis of their molecular weights. The low-molecular-weight components (< 1 kDa) typically include fatty acids and free sugars and amino acids. The majority of porewater DOC, however, is contained in the high-molecular-weight (> 1 kDa) fraction (Krom and Sholkovitz 1977; Orem et al. 1986; Burdige 2001), which consists largely of humic substances (Krom and Sholkovitz, 1977; Burdige, 2001) with minor amounts of soluble proteins, carbohydrates, and other non-humic macromolecules.

The humic and fulvic acid components of porewater DOC are believed to have significant effects on many geochemical processes in sediments, including influences on the fate and transport of organic and inorganic contaminants and on iron cycling. Aquatic humic substances can complex/bind many metallic (Cabanis 1992; Wood 1996), organometallic (O'Loughlin et al. 2000; Amirbahman et al. 2002), and organic compounds (Chiou et al. 1986; Chin et al. 1997; Perminova et al. 1999), leading to an apparent increase in the solubility of contaminants; however, the potential risks of increased solution-phase concentrations are often offset by the decreased bioavailability of many complexed/bound contaminants (Landrum et al. 1985; Hutchinson and Sprague 1987; Ortego and Benson 1992). Humic substances (and in some cases bulk DOC) are effective electron transfer mediators in abiotic and microbially mediated redox transformations of many contaminants (Curtis 1991; Dunnivant et al. 1992; Fredrickson et al. 2000; O'Loughlin and Burris 2000; Kappler and Haderlein 2003; O'Loughlin et al. 2003). Humic substances can also serve as electron donors or terminal electron acceptors for anaerobic respiration by a phylogenetically diverse array of microorganisms including iron-reducing, sulfate-reducing, and halorespiring bacteria, as well as methanogenic archaea (Coates et al. 1998; Lovley et al. 1999; Cervantes et al. 2002; Coates et al. 2002). Moreover, humic substances can act as electron mediators for dissimilatory iron reduction (Lovley et al. 1998), a key process in the biogeochemical cycling of iron in aquatic environments.

The reactivity of DOC with respect to a given process often varies with the source of the DOC, reflecting changes in its chemical and structural properties (Chin et al. 1997; Perminova et al. 1999; O'Loughlin and Burris 2000; Ma et al. 2001; and many others). Therefore, proper characterization of both the physical and chemical properties of porewater DOC is crucial for understanding its many roles in the biogeochemical processes involved in the cycling of major and minor elements and in the fate and transport of both organic and inorganic contaminants. Several studies have examined changes in the abundance and physicochemical properties of DOC in marine sediment porewater as a function of sediment depth (Orem and Gaudette 1984; Brownawell and Farrington 1986; Chen et al. 1993; Alperin et al. 1994; Burdige and Gardner 1998; Papadimitriou et al. 2002); however, similar studies of sediment porewater DOC from freshwater systems have been limited (Chin and Gschwend

1991; Chin et al. 1998), and we are unaware of any study that has examined both the abundance and properties of DOC in interstitial porewaters from lacustrine systems on the scale of the Laurentian Great Lakes. In this investigation, we measured the abundance, spectroscopic properties, and molecular weight distributions of porewater DOC, as well as the concentration of dissolved Fe^{II} , as a function of depth in sediment cores collected from Green Bay, providing insights into the nature and properties of lacustrine porewater DOC.

Materials and methods

Sediment coring and porewater extraction

Sediment cores were collected from Lake Michigan's Green Bay at Station 30 ($44^{\circ}55'62''\text{N}$, $87^{\circ}27'96''\text{W}$), northwest of Sturgeon Bay, WI, USA (Figure 1), at a depth of 27 m using a gravity corer designed to collect three cores simultaneously. Upon retrieval of the coring device, the core liners (67 mm i.d.) were removed and sealed at both ends. Within 4 h of collection, the sediment cores were transferred to a whole-core squeezer with a hydraulic extruder. The squeezer design, similar to the one developed by Jahnke (1988), incorporates a fixed top piston and a movable bottom piston. The squeezer was constructed from acrylic tubing (67 mm i.d.) and has sampling ports at various positions

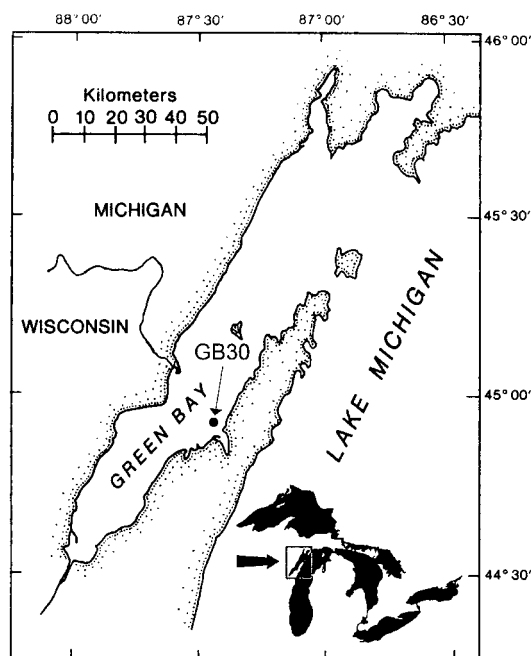


Figure 1. Location of Green Bay Station 30.

along its length. Ports were spaced 1 cm apart from 0 to 5 cm, 2 cm apart from 5 to 15 cm, and 3 cm apart from 15 to 33 cm. Each port was machined to accept a 1/4-in, 28-thread plastic Luer fitting. The fittings were connected to three-way valves. Prior to pressurizing, an acid-washed 70- μm Porex filter rod (Porex Technologies) was inserted through each fitting and into the sediment, extending to the center of the sediment core. The porous filters retain much of the particulate material but do not effectively exclude colloidal and dissolved materials. To remove any trapped air and preserve the redox status of the porewaters, the valves were flushed with porewater before sampling by gently pressurizing the core. As the core was pressurized by adjusting the bottom piston, porewaters were collected in syringes attached to the port valves. Porewater for Fe^{II} determination was collected in acid-washed plastic 10-ml syringes. The porewaters were filtered through 0.45- μm nylon membrane filters directly into plastic vials and immediately acidified to $\sim\text{pH}$ 2.0 with trace-metal-grade HCl to inhibit oxidation of Fe^{II} to Fe^{III} . Porewater for DOC, spectral, and molecular weight determinations was collected in glass syringes. The syringe tips were sealed with stainless steel Luer fittings, and the syringe barrels were secured with Keck clips. The syringes were then placed in leak-proof bags, which were subsequently submerged in water and kept in the dark at 4 °C until analysis. The redox status of porewaters stored in this manner is maintained for several weeks (Chin and Gschwend 1991); however, our analyses were completed within 3 days. Particulate material was allowed to settle by placing the syringes, plunger end down, in a water-filled beaker for 24 h prior to analysis.

DOC and Fe^{II} analysis

The DOC content of the porewaters was measured with a Shimadzu 5000 total OC analyzer, which is similar to the instrument designed by Sugimura and Suzuki (1988). Samples (10–40 μl) were introduced by direct aqueous injection onto a platinum-on-alumina catalyst heated to 680 °C in a quartz reaction tube. Prior to analysis, samples were treated with 20% phosphoric acid and sparged with CO_2 -free air for 3 min to remove inorganic carbon. The combusted organic matter was detected as CO_2 gas in a non-dispersive infrared detector. The carbon analyzer was calibrated with potassium hydrogen phthalate standards at C concentrations ranging from 0.3 to 3.0 mM.

The concentration of Fe^{II} in the porewaters was assayed in the field within hours of sample collection using the phenanthroline method (Rand et al. 1976) and a portable spectrophotometer.

Spectroscopic analysis

Spectrophotometric analyses of the samples were conducted on a Cary 1 dual-beam scanning ultraviolet-visible spectrophotometer (Varian Instruments).

Samples were placed in a 1-cm quartz window cuvette and scanned from 700 to 200 nm. Absorbance values were recorded at 280 nm (the region where π - π^* electron transitions occur for a number of aromatic moieties). Molar absorptivities were determined by dividing the absorbance by the OC content of the porewater and the path length of the sample cuvette.

Molecular weight determinations

We used high-pressure size exclusion chromatography (HPSEC) to measure both the number- and weight-average molecular weight distributions of porewater DOC. This technique is fast and non-destructive, and it requires relatively small volumes of sample. The instrumentation consisted of a Waters 510 solvent pump, a Waters 486 variable-wavelength detector, and a Rheodyne rotary injector valve equipped with a 20- μ l sample loop (Waters Associates, Milford, MA). A Waters Protein-Pak 125 modified silica column was employed for this study. The column packing was selected because of its low residual hydrophobicity and minimal ion-exchange capacity. Porewater eluents were detected at a wavelength of 224 nm. The mobile phase was composed of high-purity (18 M Ω cm) water buffered with phosphate (4 mM) at pH 6.8. In addition, sodium chloride was added as a 'swamping electrolyte' to yield an ionic strength of 0.1 M. The chromatograms were recorded using the Maxima GPC software for peak integration and molecular weight determination. Acetone was used to measure the permeation volume (V_p). The HPSEC system was calibrated with randomly coiled sodium polystyrenesulfonate (18, 8, 5.4, and 1.8 K) standards (Polysciences, Inc.). The calibration curves were used to determine the molecular weight of an analyte, M_i , at some eluted volume i . Number- (M_n) and weight-averaged (M_w) molecular weights for the humic substances and colloids were determined using the following equations:

$$M_n = \sum_{i=1}^N h_i / \sum_{i=1}^N h_i / M_i, \quad (1)$$

$$M_w = \sum_{i=1}^N h_i(M_i) / \sum_{i=1}^N h_i, \quad (2)$$

where h_i is the height of the sample HPSEC curve eluted at volume i .

Results and discussion

Sediment cores

The sediment cores were relatively undisturbed. Unidentified chironomid larvae were observed extending from the top 1 cm into the overlying water. The

color of the sediments changed from light brown in the top 4–7 cm to dark gray at depths greater than 7 cm. Outgassing was evident in the first 3 cm. Because of the varying porosity within the sediment core, different sampling ports yielded porewater sample volumes that ranged from 3 to 9 ml; typically, porewater yields decreased with depth. Although the volume of porewater recovered may be lower with whole-core squeezing than with other methods (e.g., sectioning and centrifugation), whole-core squeezing has the advantage of rapid porewater recovery on-board ship and minimal sample handling, thus reducing the potential for introducing artifacts. Orem and Gaudette (1984) showed that changes in the redox status of porewater during recovery and processing can affect the speciation of constituents susceptible to redox transformations. They reported an increase in polarity and a decrease in molecular weight of porefluid DOC when porewater was exposed to the atmosphere during sample handling. Collection of porewater with a whole-core squeezer preserves the native redox status of the porewater during collection.

Porewater Fe^{II} and DOC

The vertical profile of porewater dissolved Fe^{II} (Figure 2) exhibited increasing Fe^{II} concentrations from 3.6 μM near the sediment-water interface to 163 μM

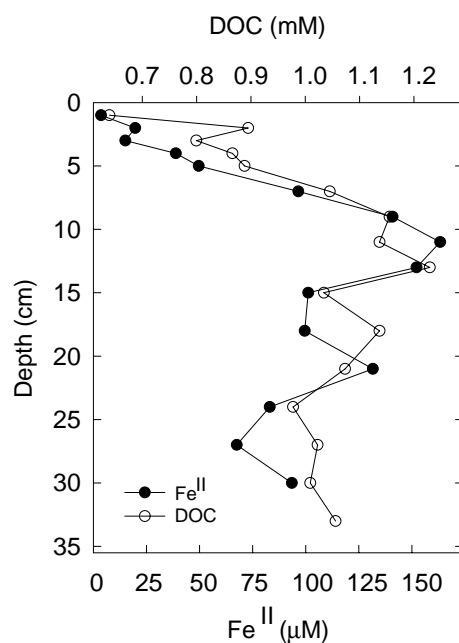


Figure 2. Profiles of dissolved Fe^{II} and DOC in porewater as a function of sediment depth.

at a depth of 11 cm, then a gradual (though erratic) decline to 93 μM at 30 cm. The initial increase in porewater dissolved Fe^{II} with depth is consistent with the change in coloration of the sediments from light brown in the top 4–7 cm, transitioning to dark gray below 7 cm, with gas pockets below 5 cm (possibly resulting from outgassing of methane, molecular hydrogen, and/or hydrogen sulfide). Similar vertical porewater profiles of dissolved Fe^{II} have been reported for surficial sediments (< 1 m in depth) in marine environments (Burdige 1993; Thamdrup et al. 1994; Krom et al. 2002). The general trend of increasing dissolved Fe^{II} with depth in sedimentary porewaters is largely the result of reduction of Fe^{III} oxides and oxyhydroxides (e.g., ferrihydrite, goethite, and lepidocrocite) and other Fe^{III} -bearing minerals by dissimilatory iron-reducing bacteria and abiotic processes.

The down-core porewater DOC concentration profile was characterized by an increase with depth from 0.64 mM at 1 cm to 1.23 mM at 13 cm, below which the concentration remained relatively constant (Figure 2). A general trend of increasing porefluid DOC with increasing depth is commonly observed with surficial sediments (< 1 m depth) from lacustrine, estuarine, and marine environments (Krom and Sholkovitz 1977; Brownawell and Farrington 1986; Chin and Gschwend 1991; Chen et al. 1993; Alperin et al. 1994; Burdige and Gardner 1998; Chin et al. 1998). The increase of porewater DOC with depth in surficial sediments is believed to result from several processes, including the accumulation of recalcitrant DOC (primarily humic substances) formed by abiotic polymerization of low-molecular-weight components of the DOC pool and microbial and abiotic degradation of particulate organic matter (Burdige 2002, and references therein).

The correlation between porefluid DOC and dissolved Fe^{II} concentrations was strong ($r^2 = 0.85$). A similarly robust correlation between porefluid DOC and dissolved Fe^{II} concentrations was observed for surficial sediment porewaters collected from a freshwater wetland (Chin et al. 1998). Ferrous iron is readily complexed by DOC (Theis and Singer 1973), and Fe^{II} –DOC complexes have been identified in porewaters from salt marsh sediments (Luther et al. 1996). Thus, the co-accumulation of DOC and Fe^{II} in the porewaters from Green Bay is consistent with the formation of Fe^{II} –DOC complexes.

Porewater spectral analysis

The π – π^* transitions for phenolic substances, analines, benzoic acids, polyenes, and polycyclic aromatic hydrocarbons occur from ~ 270 to 280 nm (Braun et al. 1988). Because many humic substances contain functional groups with structures similar to those of the above compounds, we measured the absorption (A) and determined the molar extinction coefficient (or molar absorptivity (ϵ)) at 280 nm for each of the porewater samples. The $A_{280 \text{ nm}}$ and $\epsilon_{280 \text{ nm}}$ profiles (Figure 3) of the organic matter in the porewaters generally increased with depth in a manner roughly consistent with the DOC profile

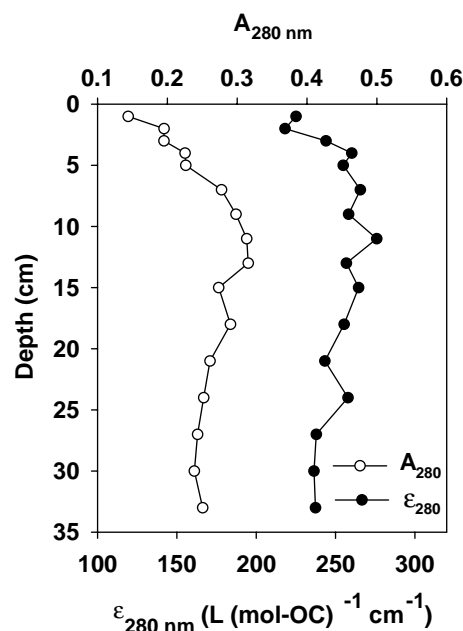


Figure 3. Profiles of porewater absorbance at 280 nm ($A_{280 \text{ nm}}$) and molar absorptivity at 280 nm ($\epsilon_{280 \text{ nm}}$) as a function of sediment depth.

(Figure 2). The $A_{280 \text{ nm}}$ values increased from 0.144 near the sediment–water interface to 0.315 at 11 cm. Below 11 cm, $A_{280 \text{ nm}}$ decreased slightly, but overall remained relatively constant. Similarly, $\epsilon_{280 \text{ nm}}$ was lower near the surface at $218.1 \text{ l (mol-OC)}^{-1} \text{ cm}^{-1}$ at 2 cm, peaked at $276.0 \text{ l (mol-OC)}^{-1} \text{ cm}^{-1}$ at 11 cm, and then decreased slightly. On average, $\epsilon_{280 \text{ nm}}$ values for these sediments were similar to values for porewaters from a freshwater wetland ($265 \pm 38 \text{ l (mol-OC)}^{-1} \text{ cm}^{-1}$) (Chin et al. 1998), but our $\epsilon_{280 \text{ nm}}$ values were substantially higher ($250 \pm 16 \text{ l (mol-OC)}^{-1} \text{ cm}^{-1}$) than those reported by Chin et al. (1991) for marine sediment porewater ($108 \pm 25 \text{ l (mol-OC)}^{-1} \text{ cm}^{-1}$).

Light absorbance has been used (with varying success) to estimate DOC concentrations in a variety of natural waters (Stewart and Wetzel 1981; Yelverton and Hackney 1986; De Haan and De Boer 1987). This approach is limited in that it only 'sees' the fraction of the DOC pool that contains chromophores that absorb light at the wavelength(s) employed. Thus, DOC measurements using these techniques may underestimate DOC concentrations by an amount corresponding to the fraction of the DOC pool that is 'invisible' at the given wavelength. We observed a strong correlation between the DOC content of the porewaters and their absorbance at 280 nm (Figure 4), thus $A_{280 \text{ nm}}$ appears to be a good predictor for DOC concentration in these waters.

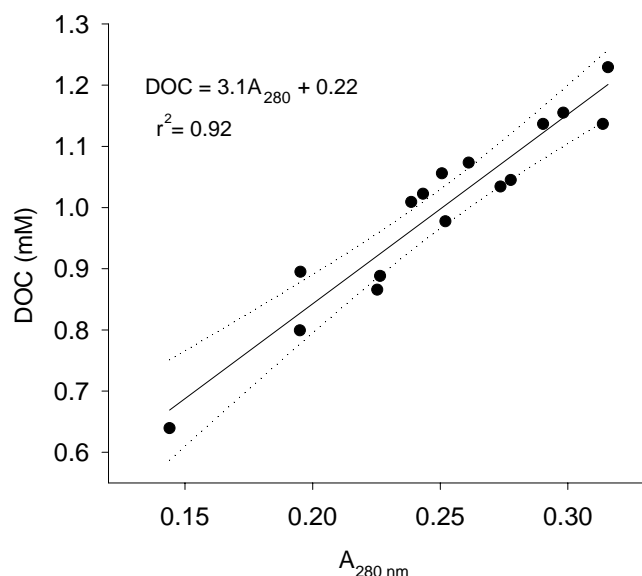


Figure 4. Relationship between DOC concentration and absorbance at 280 nm ($A_{280 \text{ nm}}$) in porewaters from GB30. Dotted lines indicate 99% confidence intervals.

Size of porewater DOC

All porewater DOC samples eluted from the HPSEC column as broad, unimodal distributions with poorly resolved shoulders and minor trailing peaks, as shown for porewater from depths of 1, 11, and 30 cm (Figure 5). The inability of the DOC to separate into discrete components defined by fractions with distinct molecular weights reflects the fact that DOC is a complex mixture of species with varying molecular weights that are difficult to resolve chromatographically; higher-molecular-weight components elute earlier than lower-molecular-weight components. The HPSEC chromatograms of GB30 porewaters differed significantly from chromatograms of porewater DOC from sediments from the northern basin of Lake Michigan (Chin et al. 1994). The Lake Michigan porewaters, collected and analyzed in the same manners as the GB30 porewaters, exhibited multimodal chromatograms with sharper, better resolved peaks. Moreover, distinct differences occurred in the porewater DOC distributions with depth in the Lake Michigan sediments: DOC in the oxic sediments was composed of relatively small organic compounds, while DOC in suboxic sediments exhibited a much larger fulvic-like peak, similar to that of Suwannee River fulvate (O'Loughlin and Chin 2000). In contrast, no significant differences in the overall DOC distributions occurred with changes in depth (Figure 5).

The fulvic-like distribution of the molecular weights of porewater DOC suggest that much of the DOC pool is composed of humic-type material.

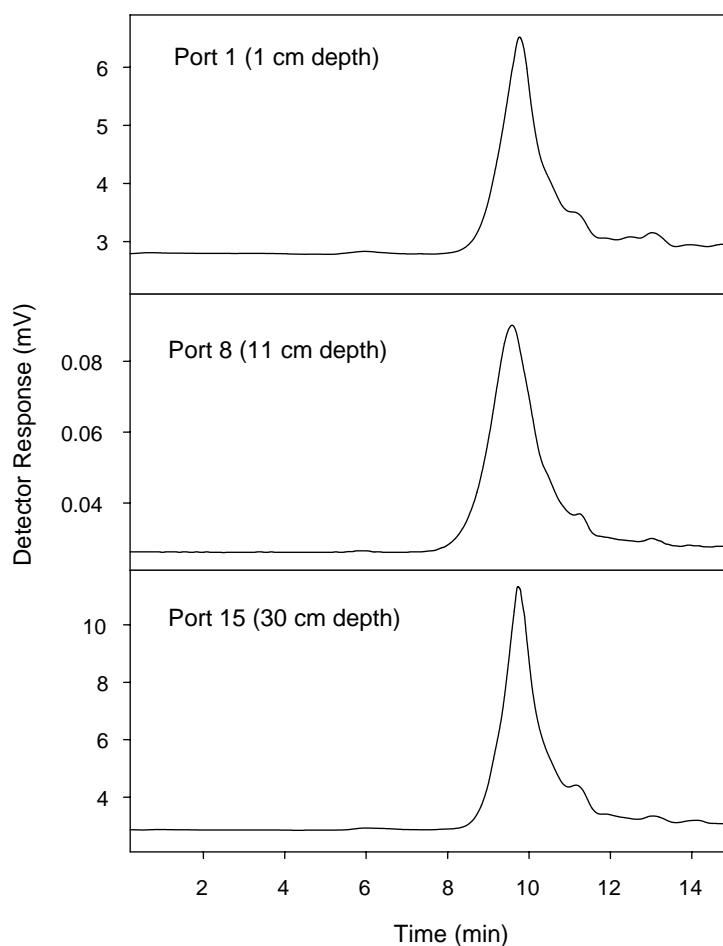


Figure 5. HPSEC chromatograms of porewaters collected at depths of 1, 11, and 30 cm in core GB30.

Indeed, the weight-average and number-average molecular weights of the porewater DOC are within the range of molecular weight distributions previously reported for reference aquatic fulvic acids (Chin et al. 1994) and for freshwater and marine porewaters (Chin and Gschwend 1991; Chin et al. 1994, 1998). Moreover, our findings are consistent with the results of previous studies indicating that the majority of porewater DOC is composed of humic substances (Krom and Sholkovitz 1977; Burdige 2001). However, the determination of molecular weight distribution by HPSEC with ultraviolet absorbance (UVA) detection may not detect significant components of the DOC pool (Her et al. 2002; Perminova et al. 2003); specifically, compounds with low absorptivities at the chosen wavelength (O'Loughlin and Chin 2001). Thus, the

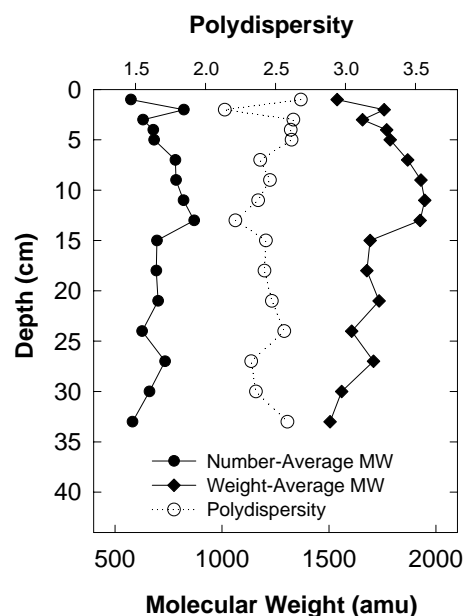


Figure 6. Profiles of porewater DOC molecular weight and polydispersity as a function of sediment depth.

dominance of humic substances in the porewaters from core GB30, as suggested by the molecular weight distributions determined by HPSEC-UVA, may be overestimated. Changes with depth in the weight- and number-average molecular weights of the porewater DOC from sediment core GB30 were subtle (Figure 6); molecular weights increased gradually from 1 to 13 cm, then gradually decreased with depth.

The molecular weight distribution of a mixture of substances can be quantified by calculating its polydispersity from the ratio of the weight-average molecular weight to the number-average molecular weight. Removal of large or small constituents from the mixture is reflected in the polydispersity. The polydispersity of the porewater organic matter was relatively low (2.13–2.68; Figure 6), suggesting that the DOC exists within a narrow range of molecular weights. No systematic change in polydispersity with depth was apparent. However, given the selective nature of HPSEC with UVA detection, the polydispersities could have been higher and more variable, because small and large non-chromophoric DOC components (e.g., polysaccharides) are not included in the molecular weight determination and thus are not reflected in the calculated polydispersity values.

Chin et al. (1994) reported a strong correlation between $\epsilon_{280\text{ nm}}$ and molecular weight for aquatic fulvic and humic acids and suggested that this correlation might provide a rapid, easy means to estimate the molecular

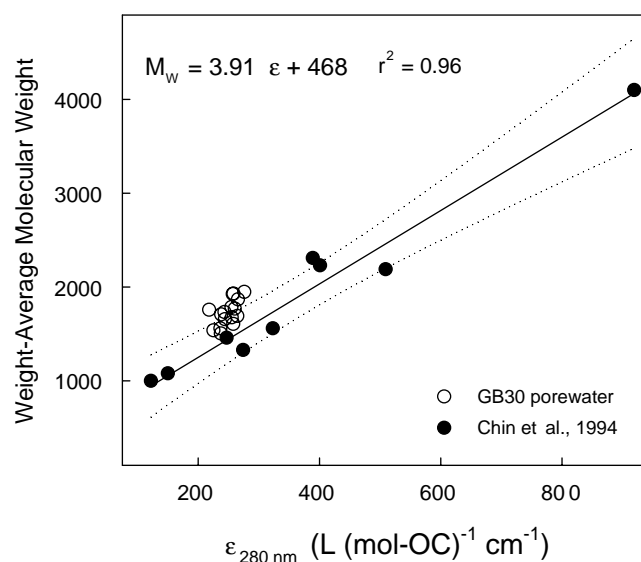


Figure 7. Relationship between weight-average molecular weight and molar absorptivity at 280 nm ($\epsilon_{280 \text{ nm}}$). Solid line indicates regression of data from Chin et al. (1994). Dotted lines indicate 99% confidence intervals.

weight of aquatic humic substances. The data from core GB30 are compared with results for reference aquatic humic substances in Figure 7. The graph indicates that using the relationship between $\epsilon_{280 \text{ nm}}$ and molecular weight for aquatic humic substances to estimate the molecular weights of the porewater DOC would yield values that are lower by 7–25% than the those determined by HPSEC. The differences between the experimentally determined molecular weights and those predicted by the model are likely due to differences in the origins of the two groups of materials. The reference humic substances are derived primarily from terrestrial plant materials (allochthonous material) and represent a defined fraction of the organic matter pool present in the sample at the time of collection, while the organic matter in the porewaters was not fractionated and is derived from both allochthonous and autochthonous materials; the waters of Green Bay support particularly high levels of primary productivity (hence the name Green Bay). Given that algae-derived humic materials are composed of organic moieties having fewer conjugate bonds than terrestrial humic substances (Harvey et al. 1983), plus the higher aromatic content of terrestrial plant materials, it is not surprising that humic substances derived from terrestrial materials would have relatively higher $\epsilon_{280 \text{ nm}}$. Although additional refinement of this relationship is required, we believe that $\epsilon_{280 \text{ nm}}$ can be used to provide a reasonable first approximation of the molecular weight of aquatic humic substances.

Conclusions

The DOC in sedimentary porewaters from the GB30 site varied as a function of changes in DOC concentration and properties with sediment depth, with the greatest variation occurring in the transitional zone between oxic and suboxic regions. Our data are unique in that ours is the first detailed study of a relatively highly resolved DOC profile in benthic porewater profile from the Laurentian Great Lakes. Because considerable care was undertaken to preserve the redox conditions within the porewaters, strong correlations were observed between DOC and Fe^{II} , suggesting the formation of complexes between these two species. Both DOC and iron play an important role in biogeochemical processes in lacustrine benthic environments (e.g., as electron donors, electron acceptors, and substrates for microbial activity, etc). Moreover, recent evidence has shown that both substances can function as active reductants in the redox transformation of organic pollutants. Thus, characterization of the nature and abundance of DOC in porewaters and its interactions with iron will greatly advance our knowledge of the role that DOC and iron play in the biogeochemical cycling of environmentally relevant compounds in benthic environments.

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